delivering 0.64 litre min^{-1}. The nozzle was positioned 350 mm above the laser crossover and each of three replicate measurements consisted of two sweeps through the spray cloud. In addition to the three oil emulsions, the droplet spectra from water, 1 g $litre^{-1}$ aqueous Agral and aqueous emulsifier at the three concentrations corresponding to the amounts present in the diluted oil ECs were measured. In addition, 1 g $litre^{-1}$ Agral was added to 10 g $litre^{-1}$ emulsions of MRO and MO to simulate the possible interaction between an emulsified oil and a pesticide containing a wetting agent.

In-flight PDPA measurements of the spray cloud showed that all of the oil-in-water emulsions increased droplet volume median diameters (VMD) when compared with water and the aqueous surfactant solution (Table 1). For example, 10 g $litre^{-1}$ MRO increased the VMD by 32% (247 to 326 μm) when compared with aqueous Agral. Emulsions of MO (10 g $litre^{-1}$) produced greater volumes of driftable droplets than similar concentrations of the two vegetable oils (2.27% *cf* 1.57 and 1.58% for ARRO and MRO, respectively). The addition of 1 g $litre^{-1}$ Agral to 10 g $litre^{-1}$ emulsions of mineral oil and MRO increased the potential of both to drift but this effect was more obvious with the mineral oil than with the vegetable oils.

Good agreement was observed between in-flight droplet-size measurements and drift data for most of the formulations. Oil emulsions and the emulsifier alone increased VMDs and decreased the proportion of driftable droplets with diameters less than 100 μm, compared with water and the surfactant solution. The surfactant generated the largest proportion of driftable droplets (5.75%) and 2.5 g $litre^{-1}$ MRO the smallest (1.34%), in accordance with their wind-tunnel drift potentials.

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Novel 1,3,5-triazine derivatives with herbicidal activity

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Abstract: New fluoroalkyl-substituted 1,3,5-triazine derivatives were synthesized and screened for herbicidal activity using a greenhouse pot test. Surprisingly, a series of 2-alkyl-4-fluoroalkyl-6-aralkylamino-1,3,5-triazines e.g. 6-(4-bromobenzylamino)-2-methyl-4-trifluoromethyl-1,3,5-triazine was found to possess strong pre- and post-emergence herbicidal activities, although the conventional herbicidal 1,3,5-triazines generally should have a 2-substituted-4,6-diamino-1,3,5-triazine structure for herbicidal activity. Our compounds show strong Photosynthetic Electron Transport inhibitory activity (PI_{50} *c*7). Although their herbicidal effect is considered to be caused by a process similar to that for the conventional 1,3,5-triazine herbicide atrazine, they can control atrazine-resistant *Chenopodium album* effectively, and will thus form promising trial compounds for new triazine herbicide design.

Keywords: 2-alkyl-4-fluoroalkyl-6-aralkylamino-1,3,5-triazines; herbicidal activity

1 INTRODUCTION

The 1,3,5-triazine skeleton is classical and one of the most interesting chemical core structures for biological activity, many triazine derivatives having been developed as agrochemicals, especially herbicides. However, most of these triazines are derivatives of cyanuric chloride simply substituted with nucleophilic reagents, and other types of triazines are not so well known. We have attempted to synthesize new types of triazine derivatives in order to find lead compounds for biological activity, starting from fluoroalkyl-substituted 1,3,5-triazine intermediates.[1] Through this approach, we found new herbicidal triazine derivatives of the type shown in Fig 1.[2]

2 EXPERIMENTAL AND RESULTS

The triazine derivatives were readily synthesized by reacting the fluoroalkyl-substituted 1,3,5-triazine in-

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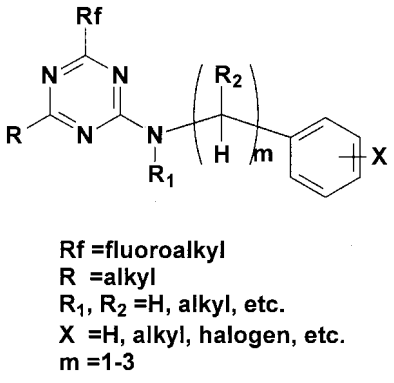


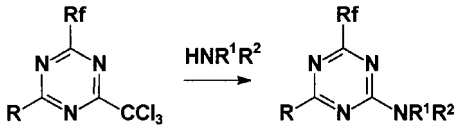
Figure 1. New herbicidal triazine derivatives.

termediates with various kinds of amine.[2] Each compound was checked for Photosynthetic Electron Transport (PET) inhibitory activity[3–5] (isolated thylakoid from spinach, $H_2O \rightarrow$ ferricyanide uncoupled by NH_4Cl) and for herbicidal activity against *Echinochloa crus-galli* (L) Beauv (two-leaf stage) as a post-emergence treatment (100 g AI ha^{-1}). Some of these compounds showed relatively strong PET inhibitory activity, and compound **10** especially had strong herbicidal activity (Table 1). From these results, the benzylamino-triazine derivatives having both methyl and trifluoromethyl substituents on the triazine ring, were found to have promising herbicidal activity.

Some (substituted) aralkylaminotriazine derivatives were synthesized to optimize their herbicidal activity (Table 2). Introduction of an alkyl group to the alpha-position of the amino group (compounds **25–30**) or elongation of the alkylene chain between the amino group and the benzene ring (compounds **23** and **24**) retained both herbicidal activity and PET inhibitory activity, but their activities were similar to, or slightly weaker than, those of the mother compound **10**. In comparing the activities of enantiomers **25** and **26**, a notable chiral recognition was observed, the (*S*)-form showing a strong activity while the (*R*)-form had no herbicidal activity. Alkylation of the secondary amino function (compounds **21** and **22**) caused complete loss of activity. From these results, favourable components for activity were considered to be $R^1 = H$ or (*S*)-alkyl, $R^2 = H$, and $n = 0$ in the general formula in Table 2.

Further synthesis was concentrated on substituted benzylamino- derivatives by reason of their strong activities and their simple structures. Pre- and post-emergence herbicidal activities against the four weeds (*E. crus-galli* (EC), *Digitaria ciliaris* Koeler (DC) *Amaranthus lividus* L (AL) and *Chenopodium album* L (CA), and PET inhibitory activities were evaluated for the compounds documented in Table 3. Favourable substituents for activity were halogen atoms or a trifluoromethyl group on the 3- or 4- positions of the benzene ring; in particular the 4-bromo derivative (compound **33**) showed better herbicidal activity than the other compounds.

Since the triazine compounds with a strong herbicidal activity show strong PET inhibitory activity (PI_{50} *c* 7), the herbicidal effect is considered to be caused by a process similar to that for the conventional 1,3,5-triazine herbicide, atrazine. However, since the new triazines have only one amino group on the triazine ring, and their molecular shapes are quite different from those of existing triazine herbicides, binding patterns of selected new triazine compounds have been evaluated in the presence of [^{14}C]atrazine. Since

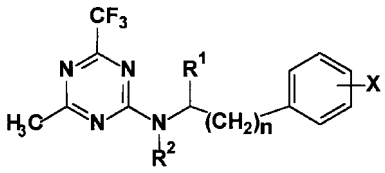


Compound	*R*	*Rf*	R^1	R^2	*PET (pI_{50}) inhibition*	*Herbicidal activity*[a]
1	CH_3	CF_3	H	H	<3	0
2	CH_3	CF_3	H	CH_3	3.80	0
3	CH_3	CF_3	H	C_2H_5	4.69	0
4	CH_3	CF_3	CH_3	CH_3	<3	0
5	CH_3	CF_3	C_2H_5	C_2H_5	3.26	0
6	CH_3	CF_3	H	C_5H11	6.37	1
7	CH_3	CF_3	H	C_8H_{17}	6.79	1
8	CH_3	CF_3	H	$C_{18}H_{37}$	4.27	0
9	CH_3	CF_3	CH_3	$C_{18}H_{37}$	<3	0
10	CH_3	CF_3	H	$CH_2C_6H_5$	6.85	5
11	C_2H_5	CF_3	H	$CH_2C_6H_5$	5.64	0
12	i-C_3H_7	CF_3	H	$CH_2C_6H_5$	4.21	0
13	C_6H_5	CF_3	H	$CH_2C_6H_5$	<4	0
14	CCl_3	CF_3	H	$CH_2C_6H_5$	5.25	0
15	CH_3	CHF_2	H	$CH_2C_6H_5$	5.69	3
16	CH_3	C_2F_5	H	$CH_2C_6H_5$	6.46	4
17	CH_3	n-C_3F_7	H	$CH_2C_6H_5$	5.29	0

Table 1. Triazine derivatives synthesized by the above reaction

[a] 0 (no effect) < 1 < 2 < 3 < 4 < 5 (complete kill).

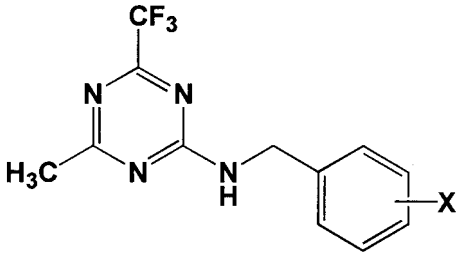
Table 2. Activities of aralkylamino-1,3,5-triazine derivatives



Compound	R^1	R^2	n	X	Activity against E crus-galli[a] Pre-emergence[b]	Post-emergence[c]	PET inhibition pI_{50}
10	H	H	0	H	5	5	6.85
18	H	H	0	4-F	5	5	6.91
19	H	H	0	4-Cl	5	5	6.98
20	H	H	0	4-tert-Bu	5	4	6.75
21	H	CH_3	0	H	0	0	4.01
22	H	C_2H_5	0	H	0	0	<4
23	H	H	1	H	3	2	5.39
24	H	H	2	H	4	5	6.75
25	CH_3(*S*)	H	0	H	5	5	6.83
26	CH_3(*R*)	H	0	H	0	0	4.55
27	CH_3	H	0	4-F	5	2	6.32
28	CH_3	H	0	4-Cl	5	3	6.69
29	CH_3	H	0	4-tert-Bu	5	2	6.66
30	C_2H_5	H	0	4-Cl	5	3	6.79

[a] On a scale 0–5, Where 0 = no activity and 5 = complete kill.
[b] 200 g AI ha^{-1}.
[c] 100 g AI ha^{-1}.

[^{14}C]atrazine bound to isolated thylakoids from spinach was displaced by addition of the triazine compounds, and the displacement was competitive, they were considered to bind to a similar, or to the same, site as atrazine. Compounds **10** (H), **32** (3-Cl) and **19** (4-Cl) could replace [^{14}C]atrazine at low



Compound	X	Pre-emergence Activity at 25 g AI ha^{-1} against[a] EC	DC	AL	CA	Post-emergence EC	DC	AL	CA	PET inhibition pI_{50}
10	H	2	3	4	5	0	0	3	3	6.85
31	2-Cl	1	1	2	4	0	0	2	4	5.95
32	3-Cl	1	3	4	5	3	5	5	5	7.21
19	4-Cl	3	5	5	5	2	4	5	5	6.98
18	4-F	4	4	5	5	3	5	5	5	6.91
33	4-Br	4	5	5	5	5	5	5	5	6.94
34	4-CF_3	4	5	5	5	1	5	5	5	7.29
35	4-CH_3	4	1	5	5	1	0	5	5	6.74
36	4-OCH_3	4	0	4	5	2	2	5	5	6.58
20	4-*t*-C_4H_9	2	4	5	5	2	0	4	5	6.75

Table 3. Benzylaminotriazine derivatives

[a] For weed species, see text.

Table 4. Phytotoxic activity of the triazine **33** against atrazine-resistant and wild-type *Chenopodium album*

		Phytotoxic activity[b]	
Compound[a]	Rate (g AI ha^{-1})	Resistant Type[c]	Wild-type[d]
33	6.25	4	5
	12.50	5	5
	25.0	5	5
Atrazine	6.25	1	5
	12.50	1	5
	25.0	1	5
	800	1	5

[a] Applied as 100 g kg^{-1} WP.
[b] On a scale 0–5, where 0 = no effect, 5 = complete kill, assessed 12 days after treatment.
[c] 2.2–2.4 leaves, 4.5 cm.
[d] 2.5–2.7 leaves, 5.5 cm.

concentration (10^{-7} M), while a relatively high concentration (10^{-6} M) of compound **31** (2-Cl) was needed. A steric factor may cause its lower affinity (unpublished results).

PET inhibitory activities of the triazine compounds were evaluated by using thylakoids from wild-form and atrazine-resistant *C. album*. The pI_{50} values for compound **33** were 7.34 and 7.43 for wild **W** and resistant **R** types, respectively, indicating the anti-resistant nature of the compound ($I_{50}\mathbf{R}/I_{50}\mathbf{W} = 0.8$). Considering this anti-resistant nature, together with the result obtained from the binding experiment, triazine **33** may have binding partners (amino acids) different from atrazine at D1 protein, as was reported for diuron.[6]

Finally, post-emergence phytotoxic activity of compound **33** was evaluated against both atrazine-resistant mutant and wild-type *C. album* (Table 4). Both the atrazine-resistant mutant and the wild-type grown in a greenhouse were well controlled by the triazine **33**, although the mutant was not killed by atrazine, even at a dose far exceeding the conventional use rate (1–4 kg ha^{-1}). The triazine **33** may be a promising alternative to atrazine where resistence to the latter exists.

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Activity of the ilicicolins against plant pathogenic fungi

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Abstract: Ilicicolins D, E, F, dechloroilicicolin D, ascofuranone and arthrichitin were isolated from the fermentation broth of *Nectria* sp (HIL Y 90 3333). The ilicicolins showed good fungicidal activity *in planta*.

Keywords: Ilicicolins; microbial metabolites; fungicidal; *Nectria* sp

1 INTRODUCTION

Fungal attacks on crops reduce harvest yields each year, and some US$5 500 million was spent in 1997 on chemical control of fungal diseases. There is a continuing need for new fungicides to provide improved levels of control and solutions to new problems, and natural products can provide novel leads for these, as exemplified by the strobilurins that led to the β-methoxyacrylates. In the course of our screening for fungicidal agents from micro-organisms, the ilicicolins (Fig 1; **1**–**4**) were isolated from a fungicidally active fermentation broth of a fungal culture of *Nectria* sp, HIL Y 90 3333. Although these compounds had been isolated previously,[1,2] their effects against plant pathogenic fungi *in planta* have not been widely reported.[3] This report describes the fermentation, isolation and fungicidal activity of the ilicicolins, along with the other metabolites isolated.

The fungal strain Y 90 3333 was isolated from a soil

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